

New Physical Evaluation Techniques

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EVALUATION may be defined as determining the effectiveness of a given material for a particular use. The field of detergent evaluation has received considerable attention in recent years. Methods have been standardized through committees of AOCS, ASTM, and other organizations. An excellent manual on "Detergency Evaluation and Testing" was provided by Jay C. Harris in 1954 (24). The general approach used may be divided into three categories: 1) preliminary measurement of basic surfactancy and stability, 2) detergency measurement using artificially soiled cloth, laboratory devices for agitation, and reflectance determinations, and 3) practical performance in the laundry. Use of radiotracers in testing was very limited.

This review covers new developments in evaluation of detergency and related properties. Topics include preliminary physical testing, fabric detergency, and hard surface cleaning.

Measurement of Key Functions

Certain functions and properties have recently been correlated with detergency and may now be considered valid criteria in detergent screening.

Colloidal-chemical properties have become more recognized for their importance, e.g., critical micelle concentration (cmc), the concentration at which surfactant molecules begin to form aggregates with concentration increase, and solubilization, the ability of surfactants in micellar state to dissolve water-insoluble substances (12). Several workers have found that effective detergency is not achieved until surfactant concentration is several times cmc, and that detergency correlates with solubilizing activity (12,15,45). Most effective solubilizers have frequently proved to be most effective soil removers, particularly when oily and fatty soils were present. Significant mathematical relationships have been established between cmc, solubilization and detergency for both hard (glass and metal) and fibrous (cotton) substrates:

$$SR_n = \frac{C_m}{a + bC_m}$$

where $SR_n = \% \text{ soil removal minus water blank}$,
 $C_m = \text{micellar weight \% concentration (total \% conc. - cmc)}$,
a and b are constants, and $1/b$ estimates maximum detergency (SR max.)

(This equation applies when detergency begins near cmc.)

$$D = K_1 S + K_2 \quad (46)$$

where $D = \% \text{ soil removal from steel at } 180F$
 $S = \text{micellar solubilization in mg. Orange OT per } 100 \text{ ml at } 180F$
 K_1 and K_2 are constants, K_1 a function of HLB and K_2 related to log interfacial tension.

An important mechanism in detergency is emulsification. Several workers have shown that oily soil removal proceeds through a "rolling up" mechanism which resembles spontaneous emulsification (23). Knowledge of emulsion technology is important in formulation of cosmetics and detergent liquids and creams.

In addition to solubilization and emulsification of liquid soils, detergency also involves suspension of solids so that in the rinsing process, they may be flushed away (25). High soil suspending action by a particular agent obviously tends to prevent re-deposition of soil.

Foam evaluation is also discussed under this heading although there is no causal relationship between foaming and detergency. However, the nature and degree of foaming by any composition determines its utility for various applications.

cmc, Solubility, Solubilization. Of several methods available for measurement of cmc (26), the dye solubilization technique (16,17) is one of the most reliable and generally applicable. Fine crystals of a water-insoluble dye are mixed in dilutions of surfactant solution spanning concentrations above and below cmc. The mixtures are settled and samples of filtered supernatant are measured for optical densities. Values are plotted graphically and intercepts are drawn to yield cmc. The cmc is defined as the point at which solubilization begins to increase rapidly with concentration of surfactant.

To perform effectively, an agent or new chemical should have a cmc value below the use concentration ($< 0.25\%$) so that micelles are available for cleaning. Addition of electrolyte builders can lower the cmc of a given surfactant, particularly anionic types, thus providing a more favorable concentration of micelles (16). Lowness of cmc, however, is not a completely reliable criterion for detergent effectiveness. Agents such as tridecanol-5 EO have very low cmc values ($< 0.005\%$) yet are ineffective because of their very limited solubility (15). The ratio of solubility to cmc apparently is a more effective measure of detergent effectiveness. Measurement of detergent solubility in aqueous systems was described by Kortland and Kooijman (40). Their method involves cooling samples with stirring in a controlled thermostatted bath until crystallization occurs, then the temperature is raised at a rate of $4C/hr$ and the temperature at which the sample becomes quite clear is noted as the clear point. This method can be employed with binary and ternary mixtures of synthetic detergents and with builders present. Clear points are characteristic of a detergent system's solubility over a wide concentration range.

Solubilization has been measured by three approaches: 1) Gross solubility of organic solvents and volumetric measurement of undissolved solvent; 2) Dye solubility; and 3) Radiotracer method using carbon-14 tagged fats.

1) Demchenko provides methods for the volumetric determination of solubilization of water in hydrocarbon solutions of surfactants, and the solubilization of hydrocarbons and polar liquids in aqueous detergent solutions (13). Apparatus is developed for solubilizes with specific gravities greater and less than the solubilizer solution. Solubilization is determined through volumetric measurement of undissolved liquid after mixing and equilibrating phases in a thermostatted water bath. Typical data show that solubilization increases with carbon chain length of fatty acid soaps.

2) Dye solubility measurement was described above under cmc. Water insoluble dyes employed are Yel-

low AB, transazobenzene, dimethylaminobenzene and Orange OT or External Orange No. 4 (26). External Orange No. 4 (1-o-tolylazo-2 naphthol) is favored because of its very low water solubility.

Evaluation of solubilizing activity of detergent candidates is best measured with fatty or oily soils as would be encountered in practice. A new radiotracer method has been developed for such measurements using carbon-14 tagged fats.

3) Radiotracer Measurement of Solubilization (18): This method consists of adding radiotagged fat, for example, glyceryl-1, 3-C¹⁴ trioleate, to a surfactant solution, stirring in a practical manner and sampling the dispersion for measurement. A "dynamic sampling flask" (Fig. 1) permits sampling with uninterrupted stirring. The stirrer is driven by the swisher-agitator action of an apparatus similar to the Terg-O-Tometer. The samples are filtered through Millipore filters to separate emulsified from solubilized fat. The solubilized fat is recovered by salting it out into a solvent while centrifuging. Aliquots are taken and, after solvent evaporation, the fat is radioassayed by applying counts to standard curves. Using this technique, the superiority of nonionics as fatty soil solubilizers was demonstrated over anionic surfactants. Nonionics solubilized up to 0.058% by weight concentration of triolein within normal wash times. This concentration of fat represents more than would arise from the washing of normally soiled articles. Optimum solubilizing action by nonionics was demonstrated at near cloud point temperatures. This correlated with detergency results where soil removal was also found maximal near the cloud point.

Emulsification and Dispersion

Emulsifying action contributes to an agent's ability to remove oily soil and retard soil redeposition. Considerable progress has been made in the emulsion field which has a bearing on detergent evaluation. The HLB system, a measure of the hydrophile-lipophile balance of a molecule, has proved effective in surfactant screening (3,4,10,11,46,67). For most nonionic surfactants, the HLB number is simply the weight % of the hydrophilic portion of the molecule divided by 5. HLB's of other surfactants are determined by equating their solubility or emulsifying action with agents of known HLB. A strongly lipophilic emulsifier has a low HLB, usually less than 10; a highly hydrophilic emulsifier has a high HLB, usually over 10.

An empirical system of HLB values has been determined for many detergents and oils. Based on its HLB value, a surfactant may be selected for a particular application, for example, for wetting, detergency or emulsification. In selection of emulsifiers, oils are assigned HLB values and surfactants having similar HLB's are screened. This approach reduces the number of agents that have to be tested.

HLB apparently has some fundamental basis. Direct proportionalities have been established between HLB and spreading coefficients (59) and HLB and the log of critical micelle concentration (61).

Becher (5) lists three ways of stabilizing emulsions: 1) lowering of interfacial tension, 2) formation of a strong interfacial film providing a barrier against coalescence, and 3) formation of an electrical double layer which is a repulsive barrier to coalescence. Electrical stabilization is particularly important in the dispersing action of ionic surfactants. Such activity for dispersion of both liquid and solid

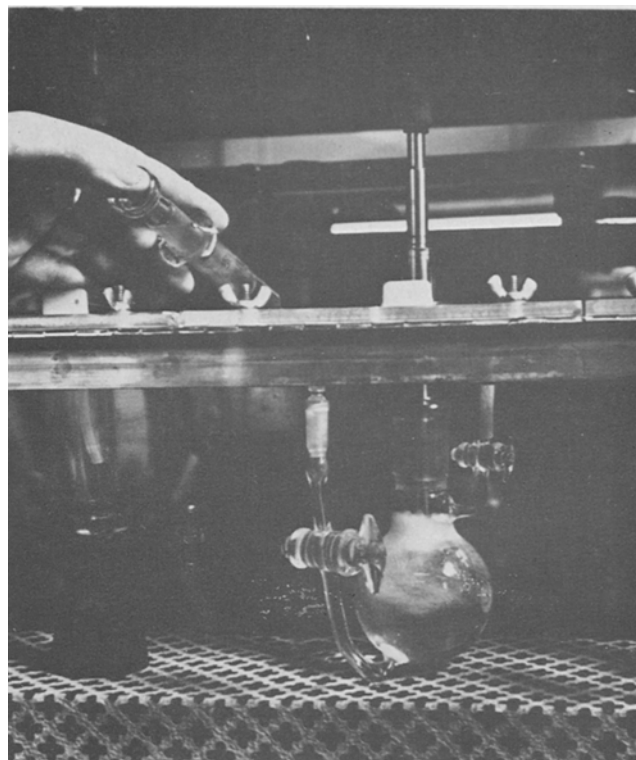


FIG. 1. Dynamic sampling flask employed in radiotracer measurement of solubilization.

soils can be measured through electrophoresis (19). The zeta potential is proportional to the electronic charge density around a suspended particle. Zeta is measured through the speed at which charged droplets or particles travel under the influence of an electric field. In measurement, the dispersion is placed in a rectangular cell equipped with two electrodes. The cell is positioned on a microscope stage. A known potential is applied and particles observed at the stationary liquid level are timed as they move across the field. This method can be useful in screening ionic surfactants and electrolyte builders for soil suspending action (25).

Peper and Rosano (53) and Zettlemyer and co-workers (68) have shown the marked influence which calcium ions have on surfactant adsorption and carbon suspendabilities. Trace amounts of calcium induce flocculation of carbon (particularly fatty acid-coated) and also increase its deposition on cotton through bridging by surfactant. Porter (55) concluded that calcium ions absorb at the interface between dirt particles and a detergent solution and hinder detergency under domestic laundering conditions. Adsorption of calcium at the fabric/solution interface results in transfer of calcium from rinse water to the next wash liquor, which can be rendered sufficiently hard to interfere with detergency, even when soft water is used for subsequent treatment.

Satisfactory washing results usually depend upon the removal of the deleterious hardness forming ions by precipitation or sequestration. It is important that an effective and reliable method be available for the screening of agents for sequestering activity. A controlled nephelometric titration method has been provided by Irani and Callis (33). The apparatus includes a temperature controlled glass vessel which houses a solution of the sequestering agent. Sodium oxalate or sodium laurate is added as a turbidity indicator of the end-point and the pH is adjusted

TABLE I
 Hardness Complexing (33)

Agent	pH	Temp °C	Sequestration per 100 g Agent	
			g Ca	g Mg
$\text{Na}_5\text{P}_3\text{O}_{10}$ (STP).....	10.5	60	9.6
Complex Phosphate $n \geq 4$	10.5	60	8.8
$\text{Na}_4\text{P}_2\text{O}_7$ (TSPP).....	10.5	60	6.2
$\text{Na}_5\text{P}_3\text{O}_{10}$ (STP).....	10.5	25	7.4	6.2
Complex Phosphate $n \geq 4$	10.5	25	5.8-7.0	5.0-5.7
$\text{Na}_4\text{P}_2\text{O}_7$ (TSPP).....	10.5	25	4.1	8.4
$\text{Na}_5\text{P}_3\text{O}_{10}$ (STP).....	9.0	25	6.7	6.0
Complex Phosphate $n \geq 4$	9.0	25	5.7-6.9	5.2-5.5
$\text{Na}_4\text{P}_2\text{O}_7$ (TSPP).....	9.0	25	2.9	6.5

to the desired level. The beaker containing the solution is placed in a nephelometer equipped with a recorder and is allowed to reach temperature equilibrium. Either 0.1M calcium or magnesium nitrate is then added automatically and periodically in cycles without stirring. In the other part of the cycle the solution is stirred. The method therefore involves alternate titrant addition and stirring with scheduled regularity. The end-point is the point at which developed turbidity does not dissipate on stirring. This method is quantitative, unbiased, and useful for selecting most effective sequestering agents. Table I shows comparative data for various phosphates in sequestering of calcium and magnesium ions.

Foam Evaluation. Dynamic foam evaluation methods (54,58,66) have been developed which provide more meaningful data than the classical, static methods. The highly developed apparatus of Reich and coworkers (58) illustrates this approach. Ten liters of an aqueous surfactant solution are placed in a 10" x 10" "Pyrex" jar which is equipped for temperature control. A self-priming centrifugal pump circulates the surfactant solution through a calibrated glass flowmeter to a jet orifice. The jet is mounted coaxially inside a graduated tube and is positioned exactly 600 mm above the solution in the jar. Timing is initiated from the instant the stream of solution impinges on the liquid surface and the foam height is recorded at intervals until maximum foam height is reached. Flow rates can be increased to magnify differences between agents or can be reduced when excessive foam is generated. Rate of foam decay is followed after the foam is generated and the circulation is shut off. This method is useful for measurement of low or controlled sudsers.

Fabric Detergency

Soil, Fabric and Water. Relevant to the intelligent evaluation of detergents for fabric washing is the understanding of the materials and problems at hand. Some very excellent contributions have been made in this field and a brief survey of these findings is appropriate.

Harris (24) has referred to soil as matter out of place. While it can't be claimed that dirt is the same all over, there are surprising similarities in soil compositions from widely differing areas (50, 51). Air-borne and ground soils were compared by Morris and Wilsey (49). The ground or clay loam soil contains higher percentages of minerals and has a higher proportion of small particles (0-2 μ) than the air borne soil. Oldenroth (50) investigated the composition and properties of laundry soil, and divided the soil into water-insoluble and water-soluble portions. According to Oldenroth, the water-soluble soil is principally from decomposed skin cells

(ca. 70%) while the remainder is dust, soot and some water-insoluble salts. The water-soluble portion contains about 20-25% salt, about 5-7% urea and about 12-15% amino acids. Skin fat serves as a glue for the dirt. Yellowed areas were found to be enriched with fats and it was concluded that oxidation of skin fats causes yellowing. The presence of residual fats is made especially noticeable on storing of fabric if the water or laundry contained iron. Walter (65) amplified these findings and also reported that skin fats accumulate lime soaps and deposition causes yellowing and unpleasant odors. Optical bleaches go unevenly on such goods thus causing yellow stains. Iron compounds catalyze resinification of the skin fats, while the iron is oxidized to Fe_2O_3 (rust).

Powe and co-workers (56,57) at Whirlpool studied the nature of problem soils accumulating on articles after repeated laundering and use. Electron micrographs were taken of natural soil in situ. It was concluded that clay particles averaging 0.1 μ in diameter are a major inorganic component of retained soil, while the accumulating organic soil is similar to sebum and hair fat. Analysis of organic residues showed that the predominant fatty acids were C_{15} , C_{16} , and C_{18} straight chain acids. More than 30% of the total fatty acids was palmitic. Most of the organic material is combined fatty acids in the form of lime soaps or esters such as triglycerides.

In summarizing, problem soils on fabrics have been identified as containing clay particulates and skin fats chiefly in ester and lime soap form. These account for the yellow-grey buildup on garments with repeated use and washing. A mixture of fat and clay should serve as a meaningful test soil.

A consideration of fabrics reveals that many new synthetic fibers have arisen in the last 15 years and these present specific problems of washability. The rise in consumption and use of synthetic fibers is given by Borghetty and Gantz (8). Synthetic fibers are characteristically hydrophobic and this affects ease of drying and soil removal and permits manufacture of wash-wear garments. Harker (23) related polarities of some fibers and soils to ease of soil removal. He concluded that the more polar the fiber, the more easily can oily soils be removed from its surface by normal detergent action. Very polar soils are most easily removed.

High static charges frequently arise in synthetic fabrics. Carbonaceous dirt is held rather tenaciously by such fabrics and does not wash out readily. This can result in the greyish tinge usually associated with synthetics or blends such as with Dacron and cotton wash-wear shirts. The problem is complicated by the usual low substantivity which most fluorescent brightening agents have for such materials. Resin treatments with triazones, epoxides and acetals have been applied to cotton and rayon fabrics to render them wrinkle resistant and usable as wash and wear garments. Such treatments can frequently make the fabric more readily soiled and less easily cleaned (48). Resin treated cotton and synthetic fabrics complicate the evaluations problems. Certainly no product should be marketed until its effectiveness with such materials is demonstrated.

Characteristics of the washing medium, particularly water hardness levels, have an important bearing on detergent effectiveness and on the appearance of the wash. Synthetic detergents as well as soaps have different performance characteristics in soft and hard

water. Problems can arise if the product does not have the capability to perform in the water hardness of a particular area.

One can formulate to satisfy the majority of the population or can distribute products of appropriate performance characteristics to particular areas. A study was made of water hardness distribution in the United States by Leenerts (42). Both urban and total population distribution indicate a peak use for the range of 101–150 ppm. The mean water hardness, ignoring home water softeners, was estimated at 135.6 ppm with a standard deviation of 90.9 ppm. Twenty-one states, including the District of Columbia, have a weighted average hardness under 100 ppm. In general, the hardest water is found in a narrow belt covering the states of South Dakota, Iowa, Illinois, Indiana and Ohio. Ideally, three water hardnesses may be employed for general performance evaluation: 1) 50 ppm for soft water areas; 2) 135 ppm for mean water-hardness, (0–135 ppm covers hardness for about 70% of population); and 3) 300 ppm for practical extreme hardness limit, (0–300 ppm includes hardness of about 95% of population).

Selection of only one hardness for testing is difficult and probably fallacious. However, it is frequently impossible, time-wise, to evaluate products at several hardness levels. We employ the expedient of using 135 ppm hardness for routine screening of new chemicals, then include 50 and 300 ppm hardness for thorough product testing prior to large scale testing.

Wetting and Wettability. It has been stated that a solution which doesn't wet, will not clean, and that wetting is a basic factor in detergent effectiveness (20). Certainly the detergent solution must be in intimate contact with the substrate in order to exert cleansing action. The converse necessity is not true. A solution which has strong wetting action will not necessarily clean. With this in mind, we may consider wetting a key factor in detergent evaluation.

Interesting new methods have been proposed for wetting evaluation. Durham and Kamp (14) developed an instrumental method which they claim is more reproducible than the usual measurements of the times required for skeins or cloth discs to sink. Three electrodes are positioned on a circular piece of cotton and bear against its surface. As the wetting solution proceeds from the control electrode to a nearby electrode, it provides a conduction path and the resulting current actuates a relay which turns on an electronic timer. As the wetting solution moves to the third electrode, a second relay stops the timer. The net time recorded is an accurate measure of the time required to wet a given area of cloth. Use of the method shows the improvement in wetting from added electrolyte builder and the difficulty of wetting cotton which contains fat and particulate matter. Wetting evaluation with soiled rather than unsoiled cotton certainly has more practical bearing even though reproducibility is a problem.

Goette (20–22) has proposed a method involving immersion of cotton discs. The 35 mm disc is introduced to the solution by means of a special immersion fork which has a sliding top. The fork is placed into a beaker containing the solution and timing is started. The watch is stopped as soon as the disc starts to sink. Activity is expressed as the concentration of surface active agent sufficient to expel air and induce sinking in 100 sec. Several cooperating countries have obtained good agreement by this method.

Perhaps the most significant development in the

field of wetting is the concept of *critical surface tension* advanced by Zisman and co-workers (6,41,52). Plotted are values for the cosine of the contact angle (θ) of solution droplets against the substrate versus surface tensions against air for the same surfactant solutions. Extrapolation is made to zero contact angle to obtain the solution surface tension required for complete wetting. A solution having a surface tension below the critical value will wet the substrate.

Soil Removal Measurement for Fabrics

Reflectometer Methods. Conventional approaches employing standard soil fabric and laboratory machines such as the Terg-O-Tometer have been refined through statistical treatments (43).

Jungermann and co-workers (37) correlated detergency performance with gas chromatographic patterns of alkylbenzene constituents of detergent actives. Presented were the typical peak heights obtained from chromatographing a desulfonated alkylate from spray-dried detergents. It was found that when the ratio of peak height -1 to peak height -2 is greater than unity, the detergency of the original built sulfonate was good; when the ratio was less than unity, detergency was poor relative to the standard. This gas chromatographic technique was recommended for use in assuring quality and product uniformity of a particular formulation. Here is an interesting use of analytical data in performance evaluation.

Wagg (63) reviewed techniques which were found most useful in the laboratory and plant for evaluating detergent products. It was pointed out that measurement of one physical property fails to completely predict the detergency action of a given product. The detergent solution must wet the cloth, remove dirt and prevent soil redeposition before the dirty wash liquor is removed. It was concluded that only tests simulating actual washing conditions were likely to supply the required information. In discussing laboratory tests with "standard" oily-carbon soiled fabric, Wagg noted the need for agreement of results with those obtained from practical wash tests. However, there is considerable lack of agreement on comparing relative performance in the laundry with natural soil to results from laboratory testing with a sample soil mixture of graphite and liquid paraffin on cotton. Good agreement was obtained when the simple graphite/liquid paraffin mixture was included in the laundry washes. Choice of "standard soil" is therefore critical, and less important are differences in mechanical action, load/liquor ratio, etc. between laundry and laboratory conditions. When the soil employed in lab tests was formulated with a *naturally* occurring oily soil and a much smaller quantity of black non-oily component for whiteness measurement, results approximated more closely those obtained with laundered articles. In these studies, dirt removal was assessed by reflectance measurement of the washed material. Compared were detergency values for various soap/sodium carbonate combinations by both reflectance and solvent extraction of oily dirt remaining on the chopped fibers. This and other data showed that correlation of reflectance measurements with oily dirt removal has been good.

Any detergents found promising by laboratory tests must finally be evaluated on a laundry scale. Sheets and pillowcases are preferred items since these frequently comprise some 50% by weight of articles processed in most laundries. Results of the test detergent are compared to a standard or reference

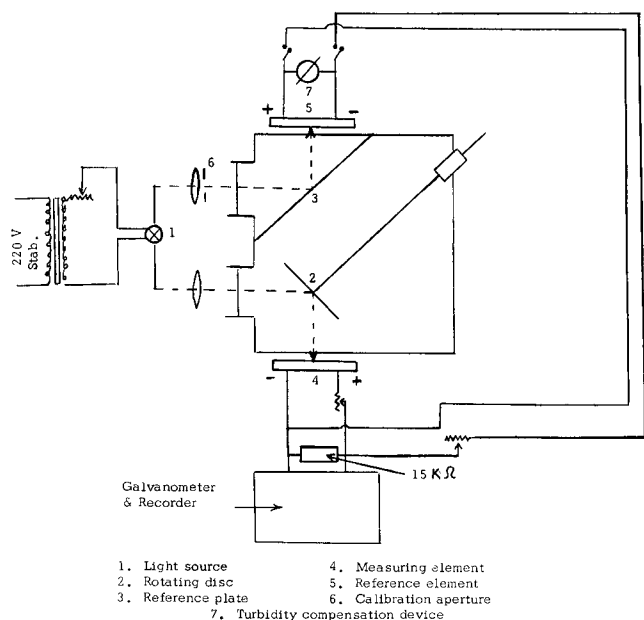


FIG. 2. Continuous measurement of whiteness during washing (simplified diagram). Bertsch et al. (7,60).

material after several washes and resoiling in home use. This method establishes differences and shows cumulative effects from small quantities of unre- moved soil and redeposited dirt. In evaluation, re- flectance measurements are made of a number of articles washed by test and reference products.

A novel instrument was developed by Bertsch and co-workers (7,60) for the direct and continuous measuring of whiteness of samples during laundering (Fig. 2). The apparatus is based on the principle that textiles in wash liquor reflect light. The main body of the instrument consists of a stainless steel housing for solution and fabric disc. Two windows are provided for introduction of light rays. The instrument functions on the basis of differential cur- rent densities. A rigid plate with an unsoiled stand- ard swatch attached is placed at 45° to the path of the reference beam. The experimental swatch is mounted on a rotating disc placed at 45° to the path of the measuring light beam. A compensating element cancels effects from increasing turbidity of the wash liquor. Recorded differential reflectance values are proportional to the soil remaining on the sample. The method is useful in kinetic studies of soil removal. By use of colored fat the method can be used to follow fat removal during the washing process.

Radiotracer Methods for Fabrics. Excellent radio- tracer techniques have been developed for evaluating fabric detergents. Utilized are radiotagged soils, fatty oils and clay, which earlier were established as natural soil components.

Wagg and Britt (64) state that 80% by weight of laundered articles are soiled with fatty excretion from sebaceous skin glands, and consequently employ a mixed fatty dirt similar in analysis to the fatty soil extracted from used underclothing and bed linen. Rates of removal from different fibers were measured for radiotagged components, radiometrically, and for included graphite by reflectance measurements. La- belled compounds used were 1-C^{14} stearic acid, gly- ceryl-tri- 1-C^{14} stearate, 4-C^{14} cholesterol, 1-C^{14} octa- decane and 1-C^{14} linoleic acid. Employed were chopped fibers of cotton, cellulose acetate, nylon, Terylene, viscose rayon, and wool. Use of chopped

fibers removed data variability because of weave characteristics. Fatty dirt mixtures were applied to the chopped fiber from chloroform dispersions. After soiling, the fibers were baked at 40°C for 20 hr. 1.5 g quantities of soiled fiber were washed four different times, then rinsed, made into 5.5 cm smooth pads and measured for radioactivity with a Geiger-Muller end window counter. Suitable controls were run with unwashed pads and corrections were made for background count. The relative efficiencies of the detergents in removing the graphite were very simi- lar to those in removing radiotagged fatty and oily matter. The hydrocarbon, octadecane, was removed more readily than glyceryl tristearate. It was more difficult to remove fatty compounds from cotton, while on the contrary graphite removal was most difficult from nylon and Terylene. Soap was the most efficient detergent although the non-ionic fre- quently equalled the soap under test conditions.

Calcium-45-tagged clay was developed as a deter- gency test soil by Hensley and Inks (32). These authors pointed out that natural soil materials may contain little finely divided elemental carbon and that natural soils or synthetic mixtures simulating natural soils appear to yield more realistic evaluations than conventional soils. The choice of clay as the test soil was based on Powe's electron photomicro- graphs showing that clay minerals constitute an important part of natural particulate soil. Employed clay was a calcium montmorillonite type which was treated with radiocalcium chloride solution until the clay had taken up about 50% of the radiocalcium initially present. The treated clay was centrifuged and washed, then dried in an oven and finally heated at 1000°C in a muffle furnace to yield a product con- taining a negligible amount of soluble or exchange- able calcium-45. The soiling suspension consisted of 1 g of tagged clay dispersed in 10 g of lubricating oil and then diluted with 75 ml of kerosene. This mixture was applied from pipet in 0.05 ml quantities at the center of 1.5-in. diameter cloth discs. Soiled discs were aged overnight, then dried in a vacuum oven. Initial counts were taken on all soiled discs, and in wash tests one soiled disc was washed with one clean disc for redeposition. After washing, the discs were rinsed, blotted, air-dried and counted using a gas-flow end-window counter. The employed laboratory washing machine consists of a cylindrical stainless steel vessel agitated with a rapid up and down motion in a constant temperature bath. A stainless steel ring clamp assembly, free to move within the vessel, carries the cloth discs. Fifty small stainless steel agitator pieces were placed on top of the soiled disc to produce necessary mechanical action. A 7-ml portion of a detergent solution was used with each pair of cloth discs. Comparative data showed distinct differences for carbon and clay soils: The carbon soil rates the unbuil nonionic as the most effective soil remover whereas the clay soil rates it intermediate between built soap and unbuil alkyl- arylsulfonate (AAS). The carbon soil indicates alka- line builders have a detrimental effect when used with either soap or the nonionic, whereas clay soil shows a distinct improvement from added alkalis, with metasilicate-built soap being most effective. Both test soils indicate a promoting action on soil removal by CMC, this effect being more pronounced with carbon soil than with clay. Considering white- ness retention and redeposition, the carbon soil data show the unbuil nonionic is most effective whereas

with clay soil it is the lowest. With carbon soil, alkali builders were detrimental in every case, the reverse being true with clay soil, and so on. The authors concluded that the tagged clay soil gives evaluations in better general accord with practical observations than those with carbon black soil.

New Concepts. Certain new concepts and approaches to evaluation of fabric detergents merit discussion. Harker (23) developed an instrument for the microscopic examination of oily soil removal from textile fabrics. The apparatus consists of a horizontal microscope assembly mounted on an optical bench. The fiber is mounted in a water-jacketed cell of stainless steel which has two glass windows. One end of the fiber is mounted using a small collar on the tip of the nozzle of a jet. The other end is clamped to a pillar which is fixed to the upper surface of one of two annual rings. The rings are moved by control outside the cell to align the fiber with the stream of liquid issuing from the jet. In this fashion, the action of water during scouring is simulated. A 35 mm camera and microscope attachment permits photographing of what is visually observed. Photographs are taken which show the "rolling up" of soil as a function of cleaning time. From these studies, Harker related fiber and soil polarities to ease of removal.

The concept of "residual work of laundering" was developed by Kling and Lange (39). These workers claimed that oily soil is chiefly removed by preferential wetting as supported by Harker's work. Oil originally spread over the fiber as a thin layer is pushed together to form spherical droplets after immersion in the washing liquor. Preferential wetting is governed by the interfacial tension σ_{AB} between the oil and the washing liquor as well as by the difference Δj between the adhesion tension for the washing liquor/fiber and for the oil/fiber interfaces. If Δj is greater than σ_{AB} , droplets are spontaneously detached. However, in most practical cases Δj is smaller than σ_{AB} , and the droplets obtain equilibrium as spherical segments with a definite contact angle. A certain amount of energy must be put in to detach the soil completely. This additional energy is termed the "residual work of washing," A_R , and is defined by the equation:

$$A_R = y\sigma_{AB}$$

where y is a function of the contact angle which in turn is correlated to Δj and σ_{AB}

The effectiveness of a detergent in removing oily soil is measured through Δj and σ_{AB} . A model system was used to illustrate the method; namely, liquid paraffin, a foil of poly- ϵ -caprolactam and a solution of sodium dodecyl sulfate. The function was related to detergent concentration. Residual work of laundering, or additional energy to effect soil release, decreases with detergent concentration. It remains to be established that this concept will yield differences between detergents which correlate with practice. Certainly we should pursue the utility of interesting new concepts as they are developed.

Hard Surface Cleaning. Any review of detergency testing is incomplete without consideration of hard surface detergents. Hard surface cleaners are applied in hand and mechanical dishwashing, tile and floor cleaners, kitchen cleansers, and window cleaners to mention only a few.

Photometric and Gravimetric Methods. Conven-

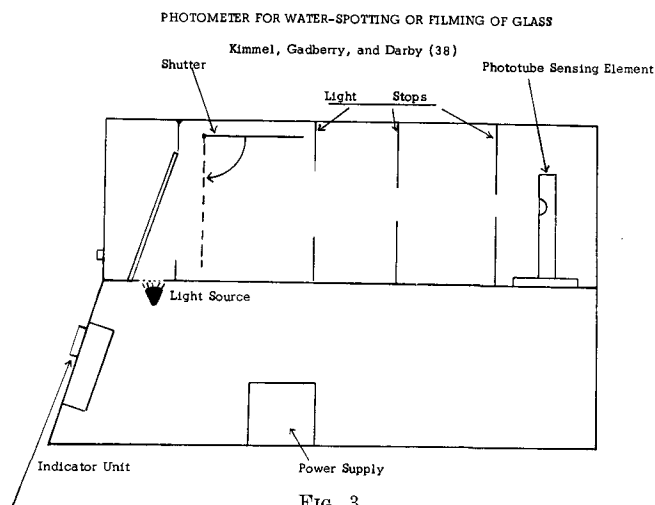


FIG. 3.

tional approaches have been newly applied and made more reliable and sensitive. Kimmel, Gadberry and Darby (38) describe a new photometric apparatus for measuring filming and water-spotting in mechanical dishwashing. Evaluation of water spotting has almost always been based on visual examination. Usual optical transmission methods are insensitive. The proposed new method is based on scattering of light (Fig. 3). A light source of 10 clear 15-w lamps is focused through a collimating slit on the specimen and comparison standard glass plates which are inclined at 10° to the light source. A shutter operates to minimize photocell fatigue and baffles eliminate spurious reflections. Matched phototubes are employed as sensing units. The signal is amplified and appears on the control panel microammeter. The test panel is automatically compared against a clean reference standard. Data were provided to show the method's practical utility in studying three important factors in dishwashing: Detergent type, machine design, and wash temperature.

An improved photometric method was developed by Liss and Hilton (44) for evaluation of hard surface, liquid cleaners. A soil mixture consisting of 20 parts metallic brown, 12 parts kerosene, 12 parts Stoddard solvent, 1 part liquid petroleum, 1 part lubricating oil and 1 part hydrogenated vegetable shortening is applied by a "doctor" blade to floor tile test strips. The soiled panels are measured for reflectance, then soaked in the wash solution and centered on a Gardner Straightline Washability Apparatus. A sponge is moved at one stroke per second across the test panel while dripping test solution at a standard rate. Washing is continued to 100 strokes, then the panel is rinsed, placed back on the apparatus and washed again to 100 strokes. After final rinsing, the panel is air dried and measured for reflectance using an amber tristimulus filter. Percent cleaning efficiency is calculated by comparison with an adopted standard. The method can be used to distinguish differences among various liquid household cleaners.

Gravimetric measurements of retained soil were employed by Mankowich (45-47) in determining fatty soil removal from steel. Test panels are dipped into the fatty soil and allowed to drain for 15 min. Soils employed were glyceryl trioleate, oleic acid and octanoic acid. In cleaning studies, soiled panels were immersed without agitation for 2 min in 1600 ml of test solution at 180F. The panels were then removed, rinsed, dried, cooled and reweighed. Weight of resid-

ual soil and percent removal were computed. Plots of detergency curves reveal the sensitivity of the method. Detergency curves have the expected sigmoidal character, that is, increase rapidly with initial concentration increase, then show relatively little detergency improvement at higher concentrations. Soil removal at cmc is relatively low, particularly for nonionics, and this finding is in agreement with results by other workers using more sensitive radiotracer methods.

Radiotracer Methods for Hard Surface Cleaning

Extremely sensitive and reliable radiotracer methods are now available for routine evaluation of hard surface detergents. Harris, Anderson and Satanek (1,2,28-31) provided a highly standardized procedure which can be used to evaluate detergent effectiveness. Employed are various carbon-14 tagged soils such as triolein, tristearin, stearic acid and algal protein. Tested substrates included glass, quartz, porcelain, steel, aluminum, polyethylene, methylmethacrylate, Nylon and Teflon. Jennings (34-36) and Bourne (9) applied similar techniques for removal of radiotagged milk films from stainless steel in dairy circulation cleaning. Substrates are cut into $1 \times 1\frac{3}{16}$ in. discs to fit into the circular counting pan. The glass discs are carefully cleaned, then frosted with carborundum powder, and finally are treated with dilute acid and water to remove inorganic contaminants. After heating to 80C, the soil is applied from a carbon tetrachloride solution using a micropipet. A spotting technique is employed to give about 10 or more monolayers of at least 46 micrograms soil per substrate disc. After aging 15 min at 80C, soiled discs are measured for radioactivity, using a gas flow counter. Results are expressed as counts per minutes and levels of between 3000 and 6000 cpm were most frequently employed in this work. The soiled and counted discs are then washed in detergent test solutions. The test apparatus is a Terg-O-Tometer which has been modified with test tube clamps to hold the soiled discs. The detergent test solution is placed in a 400 ml beaker which is surrounded by a constant temperature bath. Discs are placed in the holders and agitation is commenced at 75 cycles/minute through rotation angle of 380°. After a 20-min wash period the disc is dried and again measured for activity. Percent soil removal is calculated from initial and final counts. Plotted are detergency vs. the log concentration curves for various nonionic detergents with tristearin soil and frosted glass as the substrate. The initiation of detergency at concentrations near cmc is demonstrated by these data. Similar data are developed for other soils and substrates. The method lends itself to rapid routine screening of detergents and raw materials and has application to all phases of hard surface cleaning.

Evaluation of New Chemicals and Raw Materials

The methods discussed in this review and earlier published methods provide numerous tools for the detergent evaluator. The question inevitably arises as to which tests are employed as a product moves from a laboratory curiosity to a consumer item. A chemical supplier and soap merchandising company usually operate at different levels of evaluation though there is considerable overlapping. The chemical supplier usually performs characterization of stability, compatibility and basic surfactancy, while the soap company is more consumer oriented and performs use

tests in specific formulations. A chemical supplier may also run practical wash tests to round out data and a soap company will run preliminary screening tests of lather, surfactancy, etc. especially on new chemicals synthesized within its laboratories. The greatest difference probably lies in specificity of test formulations. The soap company usually evaluates a candidate in specific formulations, while the chemical supplier uses general formula types to show basic utility. Suggested testing of new chemicals should include most of the following measurements:

- 1). Preliminary Screening and Basic Surfactancy
 - a. Active content
 - b. Compatibility with other actives, alkalies and builders and acids
 - c. Solubility, critical micelle concentration, solubilization, surface tension properties (including spreading coefficient) and HLB.
 - d. Lime soap dispersancy
 - e. Lather and foam stabilizing effect
 - f. Fabric wetting
- 2). Detergency and Related Bench Tests
 - a. Detergency with standard soil fabric
 - b. Bench scale redeposition testing
 - c. Brightener evaluation
 - d. Softening activity and effect on rewettability (if appropriate)
- 3). Practical Testing

Multiwash laundry machine testing—soil removal by panel and test swatches, redeposition, appearance and brightness
- 4). Market Testing

Small and large scale panel testing, test markets.

In summarizing, we have presented some of the new and improved methods for detergent evaluation. Noteworthy advances have been made in areas of laboratory screening and in simulated use testing. These result from an increased understanding of detergent physical chemistry, characterization of problem soils, and more sensitive measurement techniques. Application is made of colloidal-chemical properties, clay and fatty soils, and radiotracer methods of measurement. Further improvements will develop as properties of surfactant, soil and substrate are defined, interrelated and correlated with actual performance.

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Soil Redeposition

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AN EFFICIENT detergent composition not only removes soil from substrate but also prevents redeposition. Detergents and soaps formulated with inorganic builders are highly efficient for removing soil; however, without the use of whiteness retention aid, these systems permit soil redeposition and the clean fabric areas soon show loss in whiteness. The redeposition problem first received attention when efficient synthetic detergents useful in hard as well as in soft water became available at attractive costs. Hindered originally by the whiteness retention problem, use of synthetic detergents advanced rapidly after the discovery in Germany (1) that sodium carboxymethylcellulose (CMC) is an effective anti-redeposition aid.

Investigations of the antiredeposition mechanisms have emphasized the importance of polymer adsorption on fabric and/or soil with a resulting increase in repulsion force between the two. Adsorption of CMC on cotton has been demonstrated and the exceptional efficiency of this polyelectrolyte has been related to the polymer-fabric interaction.

Laboratory, home, and commercial laundry evaluations illustrate the high level of whiteness retention achieved by use of 0.5-2.0% polymer additive in representative built soap and synthetic detergent compositions.

The extensive literature on this subject, which was ably reviewed in 1959 by Harris (2), attests to the importance of formulating detergents to prevent soiling in the washing cycle.

Because of the commercial importance of antiredeposition, a large number of water-soluble polymers differing widely in composition and functionality have been evaluated. However, despite the variety of polymers tested, only a few offer the high level of efficiency required to make them commercially attractive.

Laboratory Evaluation Procedures

A number of reliable and rapid laboratory procedures have been developed for determining the whiteness retention properties of detergent systems and for studying the interactions of detergents, builders, fabrics, and antiredeposition additives. Unless otherwise indicated, the work reviewed in this paper is based on use of cotton, commonly selected for its commercial importance as a washable fabric. Soil redeposition is usually measured by decrease in apparent reflectance when clean, white fabric is washed either 1) in a washload containing standard soiled fabric, or 2) in a detergent solution to which a controlled amount of soil has been added. The first method has the apparent advantage of similarity to end-use conditions in that clean fabric areas are washed in the presence of heavily soiled ones and the soil load is developed during the washing cycle. One criticism is that the soil load under which the antiredeposition aid must function is variable and dependent on the deterging efficiency of the surfactant. However, many investigators (3,4,5,6) have used this method successfully. Advantages cited (2) for the soil addition method include control of concentration, particle size, and state of aggregation of soil. As will be discussed later, results correlate well with end-use tests.

A variety of materials have been evaluated in the search for representative soils that can be used under controlled conditions. For the soiled fabric method, oily carbon (5,6), synthetic soils based on the analysis of street sweepings (8), and blends of the two (3,4) have been used extensively. Commercially available soiled cotton fabrics can be used for redeposition testing and are described by Harris (9).

Amorphous (10,11) and crystalline (12,13) forms of carbon black have been used as soil additives. Other synthetic soils used include raw and burnt