	Acetate	Nylon	Dacron	Orlon	Acrilan	Dynel
Scour	0.5% A 0.5% NH3	1% A 1% S 1% TSPP	1% A or N 1% TSPP	1 % A or N 1 % TSPP	1 % N	1.5% N 0.5% SA
Dye Disperse Set bath	2_% A	2% S or A 1% A 1% N	1% N 1% A 1% A <u>-</u> 2% N	0.5% A 1 % A 1 .% N 0.5% N 3 % C 1 % N	$\begin{array}{c} 0.5\% \text{ A} \\ 1 & \% \text{ N} \\ 0.5\% \text{ N} \\ 1 & \% \text{ N} \\ 0.5\% \text{ A} \\ 1 & \% \text{ N} \end{array}$	1 % A 2 % S 2 % C 2 % S 1 % A
A-Anionic Syndet; C-Cationic Syndet; N-	-Nonionic Sync	let; TSPP-Tetr	asodium Pyroph	osphate; S-Soap	; CA-Soda As	h.

TABLE II Typisal Uses of Soaps and Syndets in Scouring and Dyeing Man-Made Fibers (all percentages based on weight of fiber)

ployed. Fabric construction and available equipment often determine the scouring process.

Viscose rayon fabrics often require desizing as the first wet operation. The second operation would be scouring with an anionic detergent plus a mild alkali, such as tetrasodium pyrophosphate. Some constructions must be handled in open-width at all times and would be scoured on a jig. Other fabrics must be set with boiling water in open-width before they can be scoured in rope form.

Acetate rayon must be scoured in a neutral or mildly alkaline bath to avoid saponification of the fiber. A typical formula would employ an anionic detergent and ammonia. Blends containing acetate must be handled as carefully as an all-acetate fabric.

Typical formulas for use of soap and syndets in scouring and dyeing a few man-made fibers are shown in Table II. It must be kept in mind that many new fibers are now on the market. They may appear in a great variety of fabric structures as well as in numerous blends. A variety of scouring conditions are encountered, and many different formulas can be used. Each fiber manufacturer and the larger dyestuff companies supply scouring and dyeing procedures.

Fabrics that are only or contain grease would be scoured with a non-ionic detergent since they are most effective for removing oily soils. In the case of extremely dirty greige goods, the scour might call for 2% soap, 2% nonionic detergent, and 2%caustic soda. While this severe treatment could be used on viscose rayon, Nylon, or Dacron, it would not be used for acetate rayon and acrylic fibers. Occasionally petroleum solvents are added to the scouring bath to assist in stain removal.

Generally anionic and nonionic syndets are used most extensively. Most textile mills still use soaps however in one or more operations.

## Summary and Conclusion

The textile industry employs many millions of

# **General Detergency**

pounds of soaps and syndets for a variety of detergency problems. Cotton fabrics require soaps or syndet with alkalies to remove waxes, pectins, and other impurities which accompany raw cotton fibers. Dyed and printed cotton fabrics must be scoured with soap or syndet to remove loose color.

Raw wool fibers are scoured with a nonionic detergent or soap and soda ash as the first wet processing operation. Wool fabrics are scoured before dyeing to remove vegetable or petroleum oils applied during Wool fulling represents another large processing. market for soaps and syndets.

Man-made fibers are almost always scoured with soap, an anionic syndet, or a nonionic syndet before dyeing. Syndets are often used in the dyeing process as well as for scouring after dyeing. Inasmuch as man-made fibers are used in many fabric constructions and blends, many different formulas have been devised for scouring and dyeing.

In this discussion only the most important detergent operations for natural and man-made fibers have been considered. It must not be forgotten that the textile industry is quite diverse and many different detergent problems may be encountered. Narrow fabrics, knit goods, thread, cordage, lace, hosiery, tufted products, and hats can be cited as important segments of the textile industry. Discussion of the detergent problems in the branches of the industry was considered beyond the scope of this paper.

#### REFERENCES

- Chem. and Eng. News, 35, 124-128, August 5, 1957.
   Berger, L. D., Jr., Am. Dyestuff Reptr., 47, 179 (1958).
   Jelinek, C. F., and Mayhew, R. L., Tex. Res. J., 24, 765 (1954).
   Borgeitty, H. C., Am. Dyestuff Reptr., 43, 623 (1954).
   Speel, H. C., Schwarz, E. W. K., "Textile Chemicals and Auxiliaries," 2nd ed., Reinhold (1957).
   Schwartz, A. M., Perry, J. W., Berch, J., "Surface-Active Agents," vol. 11, Interscience Publishers, New York (1958).
   Kettering, J. H., Kraemer, R. M., U.S.D.A. Tech Bull. No. 941, August, 1947.
- August, 1947.

August, 1941.
A. Anon., Am. Dyestuff Reptr., 33, 345, 365, 385, 405 (1944).
Moore, J. L., Bell, T. E., Am. Dyestuff Reptr., 45, 679 (1956).
10. Hansen, E. C., Am. Dyestuff Reptr., 47, 155 (1958).
11. Robinson, R. D., et al., ibid., 47, 149 (1958).
12. Gantz, G. M., Am. Assoc. Soap and Glycerine Asso., Proceedings of Annual Meeting (1957).

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COAP, in one form or another, has been made and used since ancient times, and its virtues (it is one of the best detergents in soft water) and its drawbacks (chiefly its propensity to precipitate

in hard or acidic water) are well known. Because of its virtues, soap was manufactured to the extent of 1.15 billion lbs. in this country in 1957 (1). Because of its drawbacks however, and for economic reasons, soap has largely been replaced in certain uses by synthetic detergents. Total production of all synthetic types amounted to 2.85 billion lbs. in 1957(1).

Synthetic detergents are available in a variety of forms: sulfated and sulfonated alcohols, which were the first to overcome the problem of precipitation in hard water; alkyl aryl sulfonates, which origi-nated in Germany during World War I when natural fatty raw materials were scarce; various ethylene oxide condensates, which contain no sodium or other ions; and a host of other materials. It appears that any chemical manufacturer worthy of the name can make a synthetic detergent, and most



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of them do. McCutcheon (2) lists more than 1,400 surfactants manufactured by some 200 companies. Despite their great variety all detergents are structurally similar in one respect: each contains a hydrophobic (water-insoluble) group and a hydrophilic (watersoluble) group. It is the balance between these groups which gives the detergent its valuable properties.

The chemistry of surfactants is beyond the scope of the present discussion. However a simple distinction between anionic, cationic, and nonionic types

may be worth reiterating. A molecule of sodium chloride on dissolving in water will ionize to form a cation (positively-charged sodium) and an anion (negatively-charged chlorine). In ordinary soap, or sodium stearate, the long fatty stearate chain is the anion, and the compound is therefore called anionic. In quaternary salt types however the long fatty chain is the cation, and the compound is called cationic. In the case of the ethylene oxide condensates the molecule does not hydrolyze to form ions, and the compound is called nonionic. This distinction is important because the anionic and cationic types are sometimes thrown out of solution by other ionic materials.

Most anionics are incompatible with most cationics. The well-known incompatibility of ordinary soap with calcium salts or acidic materials is likewise the result of its ionic nature. The nonionics, on the other hand, are generally compatible with any materials with which they are likely to come into contact. They are however subject to a phenomenon known as inverse solubility, that is, they are more soluble cold than hot and, if the temperature is raised, a "cloud point" is reached, beyond which the solution becomes quite turbid. This does not mean they have lost their activity since only the fractions with short ethylene oxide chains are affected. These portions remain suspended and are available to perform their expected function. It has been shown elsewhere <sup>(3)</sup> that wetting efficiency does not undergo any noticeable change at the cloud point. There is also ample evidence that cloud point, as such, likewise has no adverse effect on detergent efficiency (4).

## **Detergency Testing**

Because of the importance of detergency and because of the large number of detergents on the market, the problem of selecting the best product for a given end-use is often a formidable one. Insofar as the average consumer is concerned, the final and conclusive test is, of course, a trial in his equipment and in his particular end-use. But trials on fullscale equipment are cumbersome and time-consuming and generally to be resorted to only after preliminary small-scale screening has separated the sheep from the goats and narrowed the field to two or at most three prospects. The selection of an adequate and meaningful screening test is therefore an important factor in evaluating detergents.

Scientific Approach. From a purely scientific approach it would be desirable to divide the phenomenon of detergency into a number of separate phases and measure the efficiency of the detergency into a number of separate phases and measure the efficiency of the detergent in each phase. Thus we might consider that the detergent performs at least three functions: a) allows the water to wet both the soil and the surface being cleaned; b) is adsorbed onto the surface, preferentially wetting it so that the soil is displaced; c) emulsifies oily soil and deflocculates and disperses solid soil, keeping it suspended so that it can be rinsed away. If these were the only factors and if it were possible to measure each one independently, and if the data could then be combined into suitable mathematical formulae, we might arrive at a detergency rating from which the efficiency of a detergent might be predicted.

Unfortunately detergency is such a complicated and varied process, with many possible interactions between the various soils, the surfaces, the water, and the detergent and various builders, that it is difficult to establish exactly what roles the detergent plays. Thus the simple wetting of the soil and the surface by the detergent solution involves surface tension, two interfacial tensions (solution/soil and solution/surface) and two capillary attractions. Subsequent activities depend on such factors as adsorption, micellar solubilization, deflocculation, emulsification, protective action, suspendability, and ion exchange.

It is not easy to establish which of these factors are of primary importance and which are secondary. Adam (5) put the chief emphasis on preferential wetting while McBain (6) apparently believed that the solubilizing and suspending actions are the important ones. Quite likely the demands made upon a detergent vary somewhat, depending on the exact end-use to which it is put.

Although the major factors might be known, it would still be difficult to obtain valid measurements in certain instances. Micellar solubilization, for example, is classically measured by solubilizing waterinsoluble dyes; and it is questionable whether data so obtained can be applied to solubilization of chemically dissimilar soil particles even if they were of the same size and shape as the dye particles.

Only by the continuance of research into the fundamentals of detergency can we hope eventually to obtain a complete picture of the mechanism of detergent action. Thus studies such as the work of Vold and Koneczy (9) and of Mankowich (7) on soils, and of Fineman (8) on surfaces should be combined

and extended, and eventually integrated with earlier work on the properties of detergent solutions. But such an integration, because of the number of variables, cannot be regarded as attainable in the near future.

In order to discuss the broad field of detergency, we shall consider the following factors: the soil itself, mechanism of soil removal, factors influencing soil removal, and practical detergency applications.

## Soils, Soiling, and Surfaces

When confined to detergency, soil may be defined as "matter out of place" while detergency itself can be considered as an enhanced cleaning effect caused by an agent generally described as a detergent. These are necessarily broad definitions that will apply to most of the problems.

Soils. One of the most important considerations is the nature of the soils, which is the "raison d'etre" of detergency. They may be classified according to their solubility and composition as follows:

- a) water-soluble organic and inorganic
  - 1. sugars, syrup, starch, flour, and urea
  - 2. organic acids, perspiration
  - 3. albuminous material such as blood, mucous, and egg white
- 4. inorganic salts b) water-insoluble inorganic materials
- 1. cement, plaster, soot, and lampblack
- 2. carthy materials, such as clay and silt
- c) water-insoluble organic matter
  - hydrocarbon oils such as lubricating oil and grease, fuel oil, asphalt, and tar
     paint and varnish
  - 3. animal and vegetable fats

These soils will exist separately or in varied combinations. It is apparent that the water-soluble soils are the most readily removed and generally present little or no redeposition problems. The removal of the water-insoluble types requires dispersion, emulsification, and pysicochemical adsorption effects (9). To hasten removal, alkaline builders are usually used along with heat and mechanical energy.

Soiling. Soil may be deposited on a surface by any number of mechanisms, some of which can be controlled while others, representing the more adventitious soils, are generally beyond control. In the first case one of our best examples can be found in the oiling of synthetic textile fibers. Here 0.5 to 5.0% mineral oil may be applied to assist the mechanical manipulations required to produce a varn or fabric structure. Together with the oil, which may be applied in anhydrous form or as an emulsion, there is generally included sufficient surfactant to allow for ease of removal. Other surfactants may also be present to produce antistatic effects or assistance in boundary layer lubrication. By suitable formulation and control, this type of soil may be readily removed with minor amounts of detergent and/or builder.

During various manufacturing processes, like metal fabricating, soils may also be acquired by purposeful action. These may include die lubricants, anticorrosive agents, buffing compounds, and miscellaneous extraneous soils.

However we are not always so fortunate in having conditions prefabricated to suit our proposed detergency operation. The most familiar examples of acquired soils are those dealt with in laundering and dry-cleaning operations. Little control is possible,



## A - SMOOTH SURFACE SUBSTRATE

B - BATH

S - SOIL

FIG. 1. Model for solid soils (12).

excepting in the realm of soil-preventive treatment such as starch, soluble coatings, water-repellents, and the like.

The above examples merely indicate why and how a surface may be soiled. Soiling is rarely a simple deposition of a single substance; it is usually a complex physico-chemical binding which cannot be simply expressed nor can the process whereby it is removed be expressed in simple terms.

Surfaces. The soiling process and that of its removal are greatly influenced by the nature of the surface. Surface roughness, hardness, ionic charge, wettability, and chemical reactivity, all influence these processes. Depending on the particle size of solid soils or viscosity and wetting by liquid soils, the degree of soiling can vary widely.

A soil may be held by entrapment in surface irregularities or in interstitial positions, bonded to the surface by cohesion, adsorption, or wetting effects, and held by chemical reaction with the surface. Cases of the latter are relatively rare and are generally associated with corrosion or *in situ* combination of soils like fatty acids with a metal surface. Ordinarily soiling of fabrics illustrates entrapment of solid dry soil which may also include oily constituents. Oil itself is more of a stain and, unless it is contaminated, may readily be removed by liquefaction and emulsification.

The mechanism of soil removal cannot be so readily characterized as the soil itself. A working hypothesis, based on the experience of a great many investigators, is most valuable.

## Mechanism of Soil Removal

The concept that detergency can be represented as a reversible equilibrium in which the soil:substrate complex dissociates, then reassociates to produce redeposition has furnished a basis for much experimental work and has been quite useful in the past.

 $\begin{array}{cccc} \text{Removal} & & & & \text{Redeposition} \\ \text{Substrate:Soil} + \text{Detergent Solution} & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\$ 

This theory has been used to good advantage by investigators such as Vaughan and Suter (10, 11).

However the equation is admittedly over-simplified, and Schwartz, Perry, and Berch (12) have now proposed detergency models which coincide more nearly with today's views.

In the following figures the bath B contains solutes which are either molecularly dissolved or associated colloids. These associated colloids refer to those typical surfactants which form micelles that are in thermodynamic equilibrium with the dissociated molecular or ionic form. Thus the bath is considered as a single liquid phase.

The substrate may be permeable like textile fibers or nonpermeable like glass or metal. The former will change in behavior during the washing process and complicate the process; the "hard" surfaces may also change because of adsorption effects.

The soil is generally a complex mixture of one or more solids and a liquid or oily phase. The figures assume that the liquid soil will not be selectively adsorbed by the substrate or solid soil or solubilized by the bath. Solid soils are actually of varying particle size and the figures consider only the small particles which are tenaciously held and redeposit readily, and the larger particles which are less tenacious and redeposit more slowly.

Solid Soils. Referring to Figure 1, we know that to achieve condition b it is necessary for the bath to influence S so that weak mechanical forces can separate S from A. The reverse situation would result in redeposition. A system such as this at equilibrium exists entirely in state "a" or "b". Only if the action is arrested before equilibrium will there be some soil attached and some loose in the bath.

If we relate this situation to the classical theory of lyophobic colloids, the system will exist—considering substrate A as a colloidal particle—either wholly agglomerated or wholly dispersed. There is no consideration given to a dynamic equilibrium existing between the peptized and the agglomerated state.

If we consider two different sized particles of soil  $S_1$  and  $S_2$ , then a heterodispersed system results where A plus  $S_1$  can be agglomerated and A plus  $S_2$  is dispersed when the system is at equilibrium. This is likely the situation in a practical system where very difficult-to-remove, small-particle-size soil is redeposited.

This "all or nothing" concept was illustrated by Gruntfest and Young (13) where microscopic observations showed that carbon in the absence of soap deposited onto textile fibers where addition of sufficient soap would maintain the carbon in suspension. The amount of soap titrating the soil could be related to expected detergency power.

Another excellent example has been shown by Novak in U. S. Patent 2,626,113 where a mass of asbestos fibrils form a dispersion with sodium oleate. The colloidal asbestos dispersion may be broken by dilution with water to lower the critical soap concentration. There is a minimum amount of surfactant necessary to maintain the dispersed state regardless of the amount of asbestos present. Above the minimum the amount of surfactant required is proportional to the amount of asbestos.

Of course, changes can take place in A, B, or S as they react at varied rates with one another, and the rate of dispersion of S can be altered by such factors as: adsorption of both components, penetra-



tion of both components into A and/or S, swelling, softening, or mechanical distortion of A and/or S by the bath. These are the physio-chemical factors which actually cause S and A to separate or to become attached as the case may be.

Liquid Soils. In Figure 2 the substrate A can be either permeable or not. The first hypothesis assumes that no true dynamic equilibrium exists between states "a" and "b". State "b" of I may be considered as a half dispersion—half emulsion, in which one of the dispersed phases is liquid ( $S_L$ ) and the other is solid (A). Particles of each may stick upon collision but, under conditions of no convection or agitation, a droplet  $S_L X$  will not reattach under the same conditions in which it detached from A. If X is broken into smaller droplets,  $X_1$ ,  $X_2$ ,  $X_3$ , etc., they may adhere, but in this case the original drop X has lost its identity and one criterion of the equilibrium is eliminated.

A second hypothesis considers that when an oil droplet X of  $S_L$  has been removed by the mechanism of increasing contact angle, there remains on A a thin layer of unremoved oil. Thus a monomolecular or duplex layer of oil remains strongly sorbed on the surface A.

These hypothesis are yet unproven although some



radiotracer studies have shown that oil remains on metal surfaces even though they appear clean and show no water break.

Mixed Solid-Liquid Soils. In Figure 3, the individual solid and liquid particles at V and W follow the behavior of solid and liquid soils previously discussed. In X and Z the oil could be preferentially removed, leaving the solid on the fabric, while in Y the oil could be removed with the solid still in it. This assembly might be separated in the bath, allowing the solid to redeposit. It is likely that this mechanism exists in practical laundering systems.

In these detergency models only the simplest situations have been described; actually the systems are quite complex. Factors such as the rates of each process, differential permeability of the substrates and soils, bath depletion on account of absorption, geometry, and mechanical variables have not been fully discussed. From a practical viewpoint and from the general colloid theory the models appear to have considerable advantage over the older equilibrium model.

These figures illustrate a valuable hypothesis without attempting to explain every facet of the detergent process. They serve as a systematic approach to the problem around which future investigators may design more meaningful experiments.

Some simple laboratory experiments, illustrating the influences of a few carefully controlled variables involved in the detergency process, are discussed in the following section when other variables and interactions are minimized by appropriate control tests.

## Factors Influencing Soil Removal

A major difficulty in evaluating a detergent is the fact that in most cases the composition of the soil is neither constant nor clearly defined. A large unmber of investigators have devised a variety of artifically soiled fabrics, or soil cloths, only a few of which have attained any wide acceptance. It is our purpose to point out a few of the factors that must be considered in evaluating detergents through their use.

Soil type. Many types of soil have been proposed. Carbon black is a common type; ion oxide, graphite, and even floor sweepings have been used. Some workers have classified soils as polar (e.g., manganesedioxide) and non-polar (e.g., carbon), and detergents often show a marked specificity in removing one but not the other (7).

Fully as important a distinction may be made on the basis of the amount of oil present in the formulation. Thus many published oily carbon formulations contain several times as much oil as carbon. A good oil emulsifier, which would ordinarily be effective in removing and suspending such a soil, would not necessarily be useful for removing carbon in the absence of oil.

The following commercially available soil cloths contain relatively little oil: U. S. Testing, Penn. State, Foster D. Snell, American Conditioning House. On the other hand, Testfabrics' soil cloth is definitely oily.

This is one reason why two different soil cloths will sometimes rank a series of detergents in a different order. A typical example is shown in Table I, where on oily carbon soil ordinary soap is best, followed by lauryl sulfate, alkyl phenol EO, and tall oil EO in that order. On the dry soil type the alkyl phenol EO is best while the other three are essentially equal.

Such a variation in efficiency of a detergent, depending on soil type, was strongly impressed on us some years ago during field trials in a hotel laundry. A polymeric type of nonionic, which had looked good in the laboratory when tested on dry carbon soil, gave excellent detergency on flat white work. But later it failed miserably when used on a load of greasy kitchen towels.

The choice of soil cloth type may be very important, and for complete evaluation of detergency several types must be employed. However if the soil to be encountered in practice can be adequately characterized and correlation established between the laboratory and the plant, then a single soil cloth type may suffice.

Further differences between soil cloths can arise from method of application of the soil to the cloth. For example, the soil mixture may be applied by padding, printing, or tumbling in a wash wheel. Probably more important in determining the removability is the previous history of the soil, including the medium from which the soil is applied (*e.g.*, water, solvent, or emulsion).

TABLE I					
Effect Morflow-Ometer <sup>a</sup> ,	of Soil Type 125 ° F., Distilled	Water			

0.05% Active	Testfabrics-	—oily soil	U. S. Testing-dry soil		
detergent	Reflectance	Rank	Reflectance	Rank	
Alkyl phenol EO adduct.	37.1	3	33.2 28 1	$\frac{1}{2}$	
Sodium lauryl sulfate Sodium stearate	46.1 50.0	21	$29.2 \\ 28.2$	$\tilde{2}$	

Fiber Type. Compared with the almost infinite variety of soils, the variety of fiber types is relatively limited. Nevertheless the number of fibers is increasing, and until it has been shown otherwise, we must regard each new fiber or blend as having somewhat different soil removal characteristics from the others. In the past most soil cloths were based on cotton or wool, which were the fibers in largest use. However one supplier of soil cloth has made available a series of standard soiled fabrics comprising cotton, viscose, acetate, nylon, silk, and wool, each soiled to essentially the same degree with the same type of oily carbon soil.<sup>1</sup>

In a typical experiment where swatches of each soil cloth were washed in an automatic washer of the inclined basket type with two detergents (an alkyl phenol EO and tall oil EO adduct, each suitably built), certain differences between the fiber types were readily apparent, Table II.

It is obvious that the wool is easiest to clean, viscose the most difficult. Strangely enough, cotton and viscose, which are both cellulose, show unequal ease of soil removal. If we use the data to compare the two detergents, we would say that they are equal on cotton, viscose, and silk but that the alkyl phenol is definitely superior on wool and markedly superior on nylon and acetate.

It should be remembered however that these conclusions might be true only for this particular soil type and that part of the differences attributed to

<sup>&</sup>lt;sup>1</sup> Testfabrics Inc., 55 Vandam street, New York, N. Y.

TABLE II Various Fiber Types in Automatic Inclined Basket Washer 125° F., 75 p.p.m. Water Hardness

0.5% Built detergent	Cotton	Viscose	Acetate	Nylon	Silk	Wool
Alkyl phenol EO Tall oil EO	$28 \\ 28$	$\begin{array}{c} 20\\ 16 \end{array}$	61 43	59 36	70 74	100 80
Notes: Soil cloth is 7 formulation contains 5% return to original whitene	Festfabric active ss.	s oily d detergen	earbon j t. Data	printed a is p	type. ercenta	Built age of

fiber type may actually be due to yarn and/or fabric construction.

Soil Loading. In detergent operations wherein short bath ratios are used, or in standing bath operations such as a textile plant, the effects of soil loading are most evident and most important. If the soil content of the bath becomes greater than the soilremoving and soil-suspending capacity of the detergent, loss of detergency and excessive redeposition will result. This may be remedied by increasing the bath ratio, the concentration of the detergent, and/ or more frequent discharge of the spent liquor, but all of these possible solutions can result in increased costs. However if the detergent is selected on the of its capacity for the soil in question, certain economies can be effected.

We recognize that the determination of the soilloading capacity of a detergent has not yet been systematized and fully reduced to practice, nor have all of the data shown correlation with actual operating conditions.

Nevertheless, in our brief attempts to determine soil capacity, we have made some interesting experiments. The first of these was made with several typical detergents, on Testfabrics and U. S. Testing cotton soil cloths. After the detergent efficiency of each type was established, a slurry of bentonite (a colloidal aluminum silicate clay) was added to simulate a dry type of soil, and the detergency was again determined. In a like manner U.S.P. mineral oil was stirred into the detergent baths. A large excess (15 of soil to 1 of detergent, by weight) was used in each case.

Table III shows the effect of these additives on the detergency of the four surfactant types. The detergency of the alkyl phenol EO was reduced by bentonite but was unaffected by mineral oil; for the tall oil EO adduct the reverse was true. This relationship held for both the oily and dry types of soil cloth.

With sodium lauryl sulfate the bentonite had no affect, but mineral oil produced a distinct improvement. This action is probably due to mutual solubilization and may account for the effectiveness of patented processes relating to the addition of certain amounts of free water-insoluble higher alcohols to this type of product.

Soap, represented by sodium stearate, was unaffected by either soil type.

These results could be quantitatively changed by varying the concentration of the soil or the detergent, and the choice of other operating conditions such as temperature, water hardness, etc., but it is doubtful whether the qualitative relationship would be affected.

By this illustration we do not mean to imply that the bentonite or mineral oil are representative of typical soils, but the effect of these materials exemplifies how the capacities of different detergents may vary with the soil encountered.

It may be argued that most detergents are used with builders, and that most soils are a mixture of dry and oily types. To show what can happen in such a case, a proprietary low foam household detergent, based on a tall oil EO adduct, was compared with a similar built mixture having an alkyl phenol EO adduct as the active detergent constituent.

The data shown in Table IV indicate that the detergency of the build tall oil type is reduced by oil, that of the built alkyl phenol is reduced by bentonite (as was true of the materials in the unbuilt form) while both types are adversely affected by the bentonite-oil mixture. Thus a slurry of oil and bentonite does not behave like an oily soil as its physical state would indicate, but rather each ingredient maintains its individual loading ability.

*Foam.* In many detergency operations the presence of foam can be beneficial in that solid soil may be trapped and carried away in the overflow, or the foam may merely serve as an indicator to denote the presence of adequate detergent.

However some operations suffer inconvenience because of the overflow of foam; more important, there may be an actual loss in detergency because of the cushioning effect of the foam layer. Home laundering is such an operation.

In studying home laundry detergents, a built nonionic mixture was tested in two types of washing machines. One was an automatic machine having an incline rotary basket while the other was a nonautomatic, vertical agitator type.

Suitable ballast loads of clean towels and swatches of Testfabrics cotton soil cloth were washed at  $120^{\circ}$ F. Table V illustrates the effect of foam in both machines, while the same mixture plus a defoamer produced negligible foam heights. The effect on detergency is striking. In the agitator type, where the fabric load is always submerged and not influenced by foam, both detergents are approximately equal in soil removal (% S), with the defoamed mixture being somewhat poorer when we consider its high redeposition value (% R).

In the inclined basket machine, the fabric is lifted by baffle plates and allowed to fall back into the detergent solution. Here, the cusioning effect of the foam is readily seen. The detergency for the defoamed mixture is almost half again as good as that of the

	Effect of Morfloy	TABLE Soil Loading at v-Ometer, 125° F	III 15 to 1 on Deterg '., Distilled Water	ent		
	T	estfabrics—oily s	oil	U.	S. testing-dry	soil
-	Reflectance	Change in	Reflectance	Reflectance	Change in Reflectance	
	Alone	Bentonite	Mineral oil	Alone	Bentonite	Mineral oil
Alkyl phenol EO adduct Tall oil EO adduct Sodium lauryl sulfate Sodium stearate	$37 \\ 35 \\ 46 \\ 50$		$\begin{array}{c} 0\\ -1\\ +5\\ 0\end{array}$	33 28 29 28	5 0 0 0	$\begin{smallmatrix} & 0 \\ -1.5 \\ +1.5 \\ 0 \end{smallmatrix}$

1	Testfabricsoily soil Change in Reflectance					U. S. testing—dry soil Change in Reflectance		
	Alone	Bentonite	Mineral oil	Bent. + MO	Alone	Bentonite	Mineral oil	Bent MO
Alkyl phenol EO adduct Tall oil EO adduct	40 35	-6 0	0 5	$-7 \\ -5$	33 31	-3	0 3	-5 -4

TABLE IV Effect of Soil Loading at 30 to 1 on Detergent Morflow-Ometer, 125° F., Distilled Water

regular higher foaming mix. This is one reason that manufacturers of basket-type automatic washers generally recommend the use of a low foaming detergent.

The same principles will apply to any batch operation in a drum type machine where the force necessary for detergency is cushioned by a blanket of foam.

I Test	Effect of fabrics (	TABLE Foam c Cotton S	V n Deterg ail Cloth,	ency 120° F.				
		He	ousehold	washer	type			
0.1% Active alkyl phenol EO adduct <sup>a</sup>	Inc	Inclined basket			Agitator			
	% S	% R	Inches of foam	% S	% R	Inches of foam		
Alone Plus defoamer	34 52	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		26 23	2 10	1		

Energy Input. One factor in detergency work which has not been sufficiently emphasized is that of the energy required to perform the cleaning. Primitive people, washing clothing on a river bank and beating the fabric on a rock with a smooth stick, long ago realized that the cleaning was somehow related to the amount of work expended on the fabric. This is the basic concept of which we all are conscious; we apply it qualitatively in our daily household and industrial detergent operations. Moreover in some excellent pioneering studies along this line Bacon and Smith (14) have shown by means of the LaunderOmeter that the concentration of detergent required to attain a given level of soil removal is inversely proportional to the mechanical energy applied. Yet in setting up a laboratory test, the energy level is often overlooked completely.

It is always desirable that the laboratory test correlate with actual use conditions which cannot always be duplicated on a small scale. Therefore in any test device we try to come as close as possible by proper adjustment of the variables; but in many cases the work factor is controlled merely by varying the time of operation of a machine having a fixed motion. In this fashion "all detergents get the same treatment," and most investigators are content. But this procedure can be very misleading when we consider that the work done on the fabric in the laboratory machine may be very different from that applied in the jig, open washer, or laundry machine with which we are trying to correlate.

In a brief study of this factor we have utilized a device closely resembling the Deter-Meter (15), designed and manufactured by the American Conditioning House of Boston, Mass. Our particular version we call the Morflow-Ometer.

This machine (Figures 4 and 5) consists of a variable-drive mechanism which imparts vertical

motion to a washing head over a range of 0 to 200 up and down cycles per minute. The washing head consists of a cylinder having a 100-mm. disc of soil cloth imprisoned between two screens. The distance between the screens may be set at 1, 2, or 3 cm. This assembly is oscillated vertically in 7 liters of solution contained in a stainless steel pot surrounded by a constant temperature bath. As the head moves, the soil cloth strikes the screens at the top and bottom of the stroke, which can be set at 25, 50, or 75 mm. In this manner soil loosened by mechanical action is flushed away by the detergent solution. The impact of the soil cloth against the screen is considerable, and since it strikes flat, no creases are produced on the soil cloth. Further a minor rotary motion of the cloth prevents undesirable pattern effects. Our tests are usually run at 2-cm. screen spacing, 50-mm. stroke for 15 min., at 120 cycles/min.



Fig. 4. Morflow-Ometer for detergency tests.

In one experiment soiled swatches (U.S. Testing, cotton) were washed in 0.05% of a nonionic detergent at 140° F., with variation of rate of operation of the machine (cycles/min.) but with maintenance of the same total number of cycles. A plot of reflectance of the washed soil cloth as a function of total cycles showed a family of curves, one for each rate of operation (Figure 6), with the greater cleaning efficiency being obtained at the higher rate. Since at a given point of the X-axis the number of impacts of cloth against screen is constant, it is obvious that the impact energy per stroke (which increases with the rate of operation) is responsible for the greater cleaning efficiency.

In a somewhat different experiment, ordinary soap and two typical synthetic detergents were tested in distilled water at 140° F, again with U.S. Testing cotton soil cloth. One synthetic was an alkyl aryl sulfonate, and the other an alkyl phenol EO adduct.

All variables were held constant except the speed of operation, which was varied from 25 to 200 cycles/ min. The duration of each test was 15 min., unlike the previous series where the number of cycles was held constant. The reflectance readings were plotted against cycles/min., as shown in Figure 7.

The resulting curves show that the superiority of the nonionic increases directly with the rate of operation. Thus, when we compare these detergents at 25 cycles/min., we find little difference; but at 200 cycles/min. the greater potential detergency of the nonionic has been brought out at the higher rate of operation.

It seems obvious that, to characterize detergents adequately, we should know the correct energy level at which to make our comparisons: and this should ordinarily be related directly to the operation in



Fig. 5. Detail for Morflow-Ometer.



FIG. 6. Soil removal as a function of the rate of total energy input of the Morflow-Ometer.

which the detergent is to be used. To determine the energy level of a commercial machine in terms of a laboratory device, we might attach swatches of soil cloth to fabric in process and measure the reflectance change resulting from the particular operation under consideration. The same detergent solution from actual use would then be employed in the test machine at varied rates of operation to provide a curve similar to that shown in Figure 7. The point at which the reflectance of the commercial swatches intersects the curve would indicate the correct rate of operation for the test machine. Then different detergents could be compared in the laboratory at the commercial level of operation or rate of energy input. With the work factor thus established, suitable variations in concentration could be tested and the best detergent selected for the job.

Preliminary efforts in this direction have only been partly succesful. We have recently attempted to establish energy levels of operation in terms of Morflow-Ometer cycles for our standard laboratory washing procedures in the LaunderOmeter (30 min., 20 steel balls), Laundromat (regular automatic hot cycle), and an agitator washer (20-min. wash, 10min. rinse). The same nonionic employed in the earlier experiments was used at 0.05% in the three laboratory test machines, and the resulting detergency values were compared with data for the Morflow-Ometer which had been run at varied rates of operation for periods of 15 min.

When the reflectance data of the washed soil cloth were plotted on the graph (Figure 7), it appeared that the LaunderOmeter and Laundromat had equal energy levels, corresponding to about 170 cycles/ min. on the MorflowOmeter, while the agitator washer showed a milder washing action corresponding to about 135 cycles/min.

In a similar experiment with the anionic detergent however, the agitator washer and Laundromat rated some 210 cycles/min., with the LaunderOmeter slightly lower at about 190 cycles/min. It would therefore appear that the relative energy levels of any two machines will vary somewhat, depending on the detergent being tested.

Thus, even though the principle seems sound, this preliminary attempt to establish a work factor for one machine in terms of another has given anomalous results. It is too early to state how much of the discrepancy is caused by experimental error and how

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Fig. 7. Soil removal as a function of rate of operation of the Morflow-Ometer.

much by interaction of such secondary factors as foam or the time of the scouring operation.

For the purposes of the present discussion it will suffice to say that energy is a most important variable, which must be kept in mind (along with soil type, fiber type, foam level, and other variables) in testing detergents. Only the most obvious factors have been discussed, and indeed some such as temperature have been completely slighted. However the purpose of the foregoing is served if it is recognized that "detergency" is a single name for a number of related yet dissimilar actions whereby soil is removed or displaced.

Typical detergency applications which follow indicate how diverse applications are alike in some ways and yet quite far apart in their desired effect and conditions of use.

#### **Commercial Laundry**

Equipment. Soil removal from textile fabrics and garments was at one time solely dependent on the application of mechanical energy. Any deleterious effects from such action are today lessened by the use of detergents, soaps, and alkaline builders and by elevated temperatures of softened water.

The average wash wheel in a modern laundry is a device whereby the detergent solution is moved through the fabric, accompanied by fabric to fabric friction and the squeezing action of the weight of the load. The load items are lifted by ribs or baffles in the wheel, and, in falling, their own weight provides flexing and expressions of the liquor. The reversing action of the wheel after about each six revolutions prevents tangling or balling of the garment. The size of the perforations and their dis-tribution in the shell of the machine provides varied jet action of the detergent solution onto and through the fabric. There are many variations in design and size. All have their special function and utility, but the fundamental action remains essentially 88 described.

The wash wheels may be manually controlled, but the preferred machines are fully automatic. The controls regulate the entry of the water, its temperature and depth, inject soap and/or alkali, and automatically carry out the entire operation even to a horn blast signalling the end of the wash cycle. Such automation is an economic necessity where labor accounts for so much of the operating cost. After the wash the load is hydro-extracted by centrifugal methods and either ironed or tumbled dry.

Supplies. So that we may effectively follow a discussion of the supplies and operations, Table VI shows a typical washing procedure. The most impor-

TABLE VI           Typical Washing Procedure for Family White Work           300-lb, Load, 40 x 72-in. Machine							
Operation	Time min.	Temp. °E	Water in.ª	Supplies <sup>b</sup>			
1. Break	5	100-125	6	10 gal. built soap soln., <sup>1</sup> / <sub>2</sub> lb. alkali			
2. Suds	5	130 - 140	6	5 gal. built soap soln			
3. Suds	5	160 - 170	6	4 gal. built soap soln.			
4. Suds	5	150 - 160	6	3 gal. built soap soln.			
5. Bleach	5	150-160	6	1 ½ gal. bleach (1% available chlorine)			
6 Hot rinse	1 10	150-160	12	water			

6.	Hot rinse	10	150-160	12	water
7.	Hot rinse	10	150-160	12	water
8.	Split rinse	10	135-145	12	water
9.	Cold rinse	10	110-120	12	water
0.	Sour	5	90-100	6	sour to pH 5.0
1.	Blue	10	cold	6	bluing solution
a	6 in. are ap	prox. 15	50 gal.		

<sup>b</sup> 110 lbs. soap 88% high titre, 60 lbs. alkali in 1000 gal. water, table adopted from Niven, W. W. Jr., Industrial Detergency, Reinhold Publishing Corporation, New York (1955).

tant supply is an abundance of hot soft water which is usually produced by an automatic regenerating ion exchange softening system.

The detergent generally used is a true soap, high titre for hot washing of white cotton and a low titre for warm or cold washes of colored cotton, wool, and synthetic fibers. Along with the soap, significant amounts of alkaline builders are employed. The choice of these materials is dictated by the water supply, the nature of the soiling conditions, and the type of fabric being washed. Waters high in bicarbonate require builders with a high pH; low bicarbonate water can employ somewhat low pH builders. Proportions of soap to alkali vary from 4:1 to 1:4, depending on the load conditions.

The number of sudsings depends upon the degree of soiling, fiber type, and load size. Following the suds cycle in a white cotton wash, hypochlorite bleach is generally added to provide approximately 0.01% available chlorine. This will remove the yellowing normally associated with ageing of the cotton and miscellaneous staining which may approach the fastness of dyeing. Hydrogen peroxide is also used for this purpose. After suitable rinsing, the load may be soured with sodium silicofluoride or other weak acids or weak acid salts to neutralize traces of residual alkalinity.

A bluing operation may then follow, which employs an acid dyestuff. Such dyes are not substantive to cotton, thus the load is only faintly tinted with a fugitive color; the fugitive nature of the dyestuff prevents color build-up in subsequent washings. More recently, optical bleaches have been introduced. Such materials are colorless dyestuffs which have the ability of converting ultraviolet light to visible light. The normal reflectance from a treated fabric is thus increased when viewed in a light source containing ultraviolet.

Starching or sizing may be carried out on shirts, tablecloths, and certain flatwork. Aside from appearance, the starch or sizing will protect the fibers from abrasion during use, minimize certain types of soiling, and facilitate soil removal during the next wash. The starch may be corn, wheat, rice, tapioca, or potato in amounts of 2 to 8 oz. per gallon. Starch must be swollen by cooking prior to use. This operation may be minimized and certain advantages gained by using sodium carboxy methyl cellulose, modified starches, or polymerized ethylene oxide. Some additional soil resistance and finish can be obtained by incorporation of a wax emulsion along with the starching operation.

Changes in this field are generally slower than in some of the process industries. Here the operation has been operating at a high level of efficiency for a very long time, and any process changes must not interfere with the quality of the work. Capitilization is quite high and the equipment is rather long-lived.

As with any industry employing a batch operation, there is a general desire to apply continuous operations to the process. Where the soil and/or the fabric may be classified, such as in rental linens or diapers, a continuous process would appear preferable. Raw-wool scouring in the textile field provides an example whereby the wool is fed through a series of detergent and rinse baths. The water in these systems is pumped counter to the direction of the wool while agitation is provided by rakes and squeeze rolls. Capital investment for laundering would be high in such a system, but it is almost certain that some adaptation will come in the future.

Continuous filtering of the water for reuse and purification by ion exchange is within the realm of possibility. The U.S. Army Quartermaster Corps has expressed a long-time interest in conservation of the water, especially on shipboard or in remote installations.

## Household Laundry

From the late 1800's until post-World War II soap was the backbone of all household detergents. The steady replacement by synthetic detergents began in 1932 when Dreft (16) was first marketed; another light duty product, Vel (17), followed shortly.

The early light-duty products were generally composed of some 30-40% sodium lauryl sulfate with sodium sulfate and moisture. By replacing a large part of the sulfate with complex alkaline phosphates (18), detergency approaching that of soap was attained. Prevention of deposition was accomplished by adding less than 1% sodium carboxy methyl cellulose. This addition was based on work done in Germany during World War II (19).

It was with these improvements that Tide was marketed in 1947 by Procter and Gamble. At the same time large-scale production of the sodium sulfate of alkylated benzene made possible further improvements. Along with the tripolyphosphates, CMC and fluorescent dyestuffs and silicates as corrosioninhibitors, the number of products increased and such formulations became standard. Such mixtures will clean as well or better than soap, are effective in hard water, and produce reasonably stable foams.

A typical built household laundry detergent may contain:

Ingredient	Parts	Major purpose
Sodium alkyl aryl sulfonate	20	Detergency
Fatty alcohol EO sulfate	3	Foam and detergency builder
Tetra sodium pyrophosphate	20	Water conditioning; also
Sodium tripolyhosphate	30	Soil removal and dispersion
Sodium silicate	5	Corrosion resistance
Sodium sulfate	15	Dilution
Sodium carboxymethylcellulose	0.5	Whiteness retention
Perfume, color, moisture	q.s.	Aesthetic reasons
	100%	

About the same time the use of automatic home washing machines became more widespread and in some cases, especially the end-loading types, lower foam was desirable. The answer to this problem came with All, marketed by Monsanto. Using a nonionic tall oil ethylene oxide adduct and the usual builders and additives, this product came into widespread use.

The machines in today's use are largely the agitator or revolving basket types with 8 to 10 lbs. of dryload capacity. The latter lend themselves to washerdryer combinations. It is expected that machines based on ultrasonics will make their debut within a few years. These may well require different detergents from those in use today.

Today's machines are being equipped with injectors for rinse aids or softeners which are liquid products stored in plastic reservoirs. This development will undoubtedly be extended to provide injection of a built liquid detergent. Early in 1956 such a detergent was introduced by Lever Brothers Co. Wisk is a liquid blend of anionic and nonionic surfactants combined with alkaline builders, soil suspending agent, optical brighteners, etc. This product, now in widespread use, is the forerunner of other similar products that are sure to follow.

## Dry Cleaning

Dry cleaning is technically a method of cleaning textiles by means of immersion and tumbling in petroleum distillates or chlorinated hydrocarbon solvents. The process is usually assisted by the inclusion of a detergent and moisture, accompanied by appropriate mechanical and physico-chemical procedures designed to maintain the purity of the solvent. A major difference between laundering and dry cleaning is that the latter reuses the bath after removal of the soil by distillation or absorptive filtering.

The decision to dry-clean an article is usually made by the customer, which is then followed by the plant owner's choice of methods. Often the plant may decide that a garment can best be cleaned by a careful laundering. Thus the plant operator is the final judge of how the cleaning should be accomplished, and he is in the postion of guaranteeing a clean garment regardless of the method chosen.

There is such a diversity of factors involving the choice of methods that clear-cut rules cannot be established. Guiding principles established by textile research and plant experience have enabled operators to make the proper choice. In general, fibers like wool and rayon become plastic and swell in the presence of water, especially if it is hot and alkaline. These are best dry cleaned. In addition, some fibers will take to laundering, but the dyestuffs are too fugitive or the combination of fibers and/or fabrics dictates the more gentle dry-cleaning. There has been a concerted effort among plant operators and their trade associations for more complete cooperation with garment houses and textile mills to promote proper labelling. Evidence of some success in this regard is the common label "dry-clean only." In fact, the newer silicone woolen finishes add "rinse in clear solvent." Progress is slow but steady.

Soils encountered in dry-cleaning cover the full range of oil-soluble, water-soluble, and the insoluble soils alone or in varied combination. The more obviously soiled areas may require a prespotting operation where treatment with solvent, detergent, water, enzymes, and steam are not uncommon.

Equipment. The equipment is basically the same as in laundering, excepting that means of filtering and recovering the solvent is provided. The washer is generally an end-loading type with the usual rotating baffled shell in which the garments are tumbled through solvent. A pumped filter line is arranged so that the solvent may be continuously filtered. The centrifugal extractor and tumble driers are arranged to allow recovery of the solvent, which is piped back to the washer. If the extractor is equipped with a clear-solvent spray rinse, this along with the condensed solvent from the drier acts to replenish the used solvent in the machine.

Solvent. The average self-contained unit in a local dry-cleaning establishment utilizes perchloroethylene while the larger, higher volume, more remote plant will use a petroleum solvent such as Stoddard Solvent. Some characteristics of these materials are listed as follows:

	Perchlor	Stoddard
Chemical formula	C 2 Cl 4	saturated hydrocarbons
Boiling point (° F.)	250	300-375
Specific gravity	1.6	0.80
Pounds/galon	13.55	6.54
Flammability	No	Yes
(million gallons)	7	115

The petroleum solvents are cheaper per pound of cleaning, allow larger loads, are relatively stable and noncorrosive, and are less toxic than the synthetics. The advantages for synthetics, which include carbon tetrachloride and perchloroethylene, are nonflammability (allowing fewer zoning restrictions), shorter cleaning cycles, less heat required for drying, and greater solvent action on greases, paints, etc. (about 10 times that of petroleum types).

Detergents. The detergent is expected to increase removal of inert solid soils, prevent redeposition, increase removal of water-soluble soils, reduce linting, and solubilize water in certain systems. While the detergent alone cannot guarantee the success of the entire operation, a poor detergent can make other precautions worthless. A detergent capable of keeping soil in suspension until the filter can remove it is essential in addition to maintenance of proper humidity in some systems.

Major types of detergents include soaps, anionics, and nonionics. The true soaps have the best soilremoval and suspending power but are not able to pass through the filter and tend to increase the fatty acid content of the solvent. Because of this they are relegated to use in fresh-soap-to-each-batch systems.

The anionics are the most popular types. In addition to their expected performance properties, their concentration in the bath can easily be determined by a simple anionic-cationic titration, using an indicator like bromphenol blue in chloroform. . The first types used were the petroleum sulfonates or mahogany soaps. These sodium salts of napthene sulfonic acids are soluble in the solvent and will pass through the filter. Thus they are operable in the charged system where .5 to 4% detergent by volume is continuously maintained. By preference an operator can keep .75 to 1% for a mild charge which requires no rinsing; a heavier charge of 2 to 4%may make rinsing desirable or mandatory.

Other anionics like alkyl aryl sulfonates and sulfonated or sulfated amide and ester types of detergents are used in the same manner although they may be used at higher concentrations without requiring a rinse.

Nonionics may be the alkyl aryl polyglycol ethers and the alkylolamines. These are applicable in the charged systems, but their analysis is difficult. Control is best achieved by mixture with anionics.

There are some operators who will use a freshsoap-to-each-batch approach while using a charged system. Here the detergent may be added with each batch; the amount is calculated to level off at 5 to 6%. The drag-out loss and fresh or distilled solvent additions will determine the amounts to add.

Filter Aids. The filter powder in universal use is a diatomaceous earth. This is precoated onto the filter screens or bags and added with each load at a rate of two pounds per 100 pounds of garments. This prevents sliming over the filter, which occurs if the porcedure is skipped even once.

Sweeteners are similar except that they are highly absorptive because of treatment with magnesium or aluminum silicates. These tend to remove soluble impurities which would normally pass through the filter cake. They are especially effective in removing free fatty acids and other odor-producing compounds. In general, most systems will operate acceptably with only the filter aid.

Activated Carbon. To remove residual odors and dyes which become dissolved in the solvent, activated carbon is applied as an after-coat on the filter. About two pounds are added to an unloaded wheel along with about half a pound of filter aid for each 1,000gallon-per-hour of filter capacity. Emergency additions on account of increased dye loading are made by adding a carbon-solvent slurry to the button trap.

Water. Originally water was added by accident on wet days or by carry-over from the prespotting operation. Today most systems have automatic controls which maintain the relative humidity above the solvent between 70 and 85%. Some of these devices are based on conductivity and are used in the filter line, others draw vapor from the washer over a gold leaf, humidity-sensitive plate. The amount of water called for is dependent on the condition of the load and the type of fiber being cleaned.

The water assists in the removal of water-soluble stains and reduces the amount of spotting. It has been so successful in this respect that most cleaners confine prespotting to obviously difficult spots or stains. After processing in a water-containing system, only the most stubborn spots remain for spotting operations. The charged system with 4% detergent carries a reservoir of water held in the solvent which insures sufficient humidity at all times. The equilibrium conditions in the wheel work in both directions. If too much water is introduced with the load, the

detergent will pick it up until proper humidity is indicated. In this event the electronic control will not add water.

There is continuing research in this field by the various suppliers and by the National Institute of Dry Cleaning, and it is reasonable to expect that the future will show developments as significant as those in the recent past (20).

## Dishwashing

Mechanical. There are several differences in procedure between home and restaurant machine dishwashing. In the home the detergent solution is used once on a stationary load and discarded. In commercial operations the dishes are moved through the machine where detergent solution is sprayed over them. The detergent solution is used repeatedly. Its concentration is maintained by means of an electronic dispenser, which is governed by conductivity. Another difference exists in the rinse temperature. In the restaurant the water is usually near 180° F., which is hot enough to affect some sterilization; in the home a maximum of 140-150° F. is used.

Other than the differences mentioned, the two operations are esentially the same for dishes and glassware. Restaurants generally have separate facilities for silverware and cook pots.

Detergents for dishwashing are blends of alkaline salts. The following composition is typical: 35 parts sodium tripolyphosphate, 45 parts sodium metasilicate, and 20 parts sodium carbonate. A pH of 10.5 to 12.0 is desirable.

The polyphosphates condition the water, reduce haze, and promote wetting and soil displacement. Portions of this ingredient may be replaced with trisodiumphosphate to build alkalinity. The silicate contributes to dispersion and suspension of soil as well as inhibits corrosion of metals. Carbonates act as fillers and add to alkalinity. However they tend to build up haze, hence their content is held to a minimum.

At concentrations of 0.25 to 0.5% the detergent is expected to soften the water, remove and emulsify soil ,and leave the surface of the load items completely wetted so that the rinse will sheet off without "water break." In this state the work will dry rapidly with a minimum of spotting.

In commercial installations, water sheeting is further promoted by injecting surfactant into the rinse water-line. This surfactant, which must be low foaming to prevent interference with machine operation, is generally present at only 0.003% to 0.005%in the rinse water (21).

Silverware is usually handled separately in a soak tank, followed by a spray wash. The load baskets are then manually dipped into a rinse-aid solution. Here the rinse aid receives no extreme agitation and may be a relatively high-foaming type.

For home use 2 to 5% of surfactant is incorporated into the alkali blend to provide water sheeting. The surfactant also acts to prevent soil deposition onto glasses which are included with the load. Most household machines use water alone for the rinses although the newer models feature an automatic rinse injector on the door. This device adds 0.005% of liquid surfactant into the final rinse to insure improved drying and appearance.

Manual. Detergents for this use may be the powd-

ered products normally recommended for fine laundering or especially formulated liquids. Both types are used in restaurant and home dishwashing. Restaurant washing is generally followed by a sterilizing rinse in hypochlorite or quaternary ammonium germicide solution.

The powdered products are typically a blend of alkyl aryl sulfonate, sodium tripolyphosphate, and sodium sulfate, such as are discussed under home laundry detergents. Silicates and ortho phosphates are not used because they are too alkaline for hand operations.

Liquids have taken the major market for home use. A typical product may be based on 35-40%active solution containing 23 parts of sodium alkyl aryl sulfonate slurry solubilized by 10 parts of an alkyl aryl polyether alcohol with 5 parts of lauric diethanolamide added as a foam stabilizer and emollient. Viscosity may be adjusted with small amounts of isopropyl alcohol and hexyglene glycol, with perfume or coloring added for aesthetic reasons. Other formulations sometimes employ the triethanolamine or ammonium salts of lauryl sulfate, sulfated alkyl aryl polyether alcohol, or alkyl aryl sulfonate as the detergent.

For use 0.05 to 0.10% solutions are prepared by measuring capfuls into a dishpan. At this level, detergency is excellent, and there is copious foam which is stable in the presence of soil.

Test Methods. Materials intended for use in mechanical dishwashing detergent formulations are usually evaluated in a small restaurant machine or a selected household appliance. Efficiency is evaluated by removal of food spoils, speed of drying, and presence of spots or haze on the load items. Committees of the Chemical Specialties Manufacturer's Association (CSMA) have published a spotting and filming test and, in addition, a test for over-glaze removal. This same group has an active committee for evaluating foaming properties (21).

Hand dishwashing evaluations have been made by washing soiled plates until the foam subsides, the number of plates so washed is a direct indication of efficiency. This test is also the subject of a current CSMA committee. Other industry tests rely on foam titration with increments of soil.

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### REFERENCES

REFERENCES
1. Snell, F. D., Ind. Eng. Chem., 50, 41 (1957).
2. McCutcheon, J. W., "Synthetic Detergents and Emulsifiers--Jp to Date," III., MacNair-Dorland Company Inc., New York, 1955.
3. Wolfrom, R. E., and Nuessle, A. C., Text Res. J., 22, 246-53 (April 1952).
4. Wolfrom, R. E., and Nuessle, A. C., Am. Dyestuff Reporter, 42, 753-61 (1953).
5. Adam, N. K., "The Physics and Chemistry of Surfaces," 3rd ed., p. 201, Oxford University Press, London, 1941.
6. McBain, J. W., Advances in Colloid Science," I. (Kraemer, ed.) New York, Interscience Publishers, 1942, p. 99.
7. Mankowich, A. M., Ind. Eng. Chem., 44, 1151 (1952).
8. Fineman, M. N., and Kline, P. J., J. Colloid Sci., 8, 288-99 (1953); Fineman, M. N., Soap and Sanit. Chemicals, 29, No. 3, 50-3, 114 (1953).
9. Niven, W. W. Jr., Fundamentals of Detergency, 1st ed., Reinhold Publishing Corp., New York (1950).

Vaughan, T. H., Vittore, A., and Bacon, L. R., Ind. Eng. Chem., 33, 1011 (1941).
 11. Vaughan, T. H., and Suter, H. R., J. Am. Oil Chemists' Soc. 27, 249-257 (1950).
 12. Schwartz, A. M., Perry, J. W., and Berch, J., "Surface-Active Agents," vol. II, Interscience Publishers, New York, 1958.
 13. Gruntfest, I. G., and Young, E. M., J. Am. Oil Chemists' Soc., 26, 236-238 (1949).
 14. Bacon, O. C., and Smith, J. E., Ind. Eng. Chem., 40, 2361-2370 (1948).
 15. Wollner, H. J., and Freeman, G. S., Am. Dyestuff Reptr., 40, 693 (Oct. 1951. (Deter-Meter is a registered trademark of American Conditioning House Inc.)

American Hyalsol Corp. (Procter and Gamble and du Pont jointly owned and licensed under U. S. Patents to Beitsch: U. S. Patent 1,968,793, 1,968,797 [1934] and 1,993,431 [1935]).
 17. Colgate-Palmolive.
 Byerly, D. R., U. S. Patent 2,486,921 (1949).
 Hohart Publishing Company, Washington, D. C.
 Putlon, G. P., Alexander, J. C., Lloyd, A. C., and Schwartz, M., A.S.T.M. Bulletin TP153, September 1953.
 Wilson, J. L., Mizuno, W. G., and Crecelius, S. B., Soap and Sanit. Chemicals, 34, No. 2, 48-52, 170 (1958).
 Proceedings of the Chemical Specialists Manufacturer's Assoc-iation Inc., 43rd Mid-Year Meeting, May 1957, New York, N. Y.

# **Cleaning in the Metal-Processing Industry**

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formidable task. Still greater difficulties arise in

attempting to devise methods of laboratory evalua-

tion capable of predicting

the metal-finishing indus-

try is no exception and is

further subject to complications which are some-

what specific to that field.

The soils involved have

often resulted from prior metal-processing. With

proprietary products, such

as drawing compounds,

The evaluation of cleaning materials employed in

field results.

 $\neg$  HE BASIC OBJECTIVE of every cleaning operation is to remove soil efficiently while not exceeding tolerable limits of attack upon the substrate. Translation of this simple statement into a list of practical requirements adequate either to define efficiency of soil removal or limits of attack can be a



rust-inhibiting oils, etc., a variety of soil conditions L. R. McCoy can exist among plants performing the same metal-working operation. Another distinction lies in the fact that cleaning procedures in this industry are followed by subsequent finishing operations which differ widely in their requirements for surface cleanliness and in which constituents of

the cleaning materials can themselves serve as soils. Some idea of the scope of metal finishing and its cleaning requirements can be gained from an examination of Table I in which the principal variables are listed. Not included are certain metals now produced in small quantities, which, in the following years, may become as important as some shown here. Ultrasonic cleaning, which would not have appeared a few years ago, is now assuming greater importance. The list cannot therefore be regarded as complete and unchanging and serves only as a partial example of current practice.

The metal surfaces, important from the standpoint of limiting the cleaning compositions which can be employed without excessive corrosion, are equally important in the sense that they can become an integral part of the soil either in finely divided metallic form or by reaction with the other soil constituents. The soils derived from a given metal-working operation,

such as drawing, can vary from simple soap films removable by hot water to coatings containing pigments, oils, and additives which cling to the metal surface during severe forming operations and often, unfortunately, during the subsequent cleaning procedures. Since it is common to perform more than one operation in the course of fabricating parts, mixtures of soils frequently occur.

The manner in which cleaning compounds are employed differ primarily in their use of detergent, solvent, chemical, electro-chemical, and mechanical effects, whichever is more effective. Economic aspects, weighed against the time available for cleaning, and the degree of ultimate cleanliness required are also involved.

At the same time the manner of use places requirements upon the cleaning material not directly related to cleaning ability but no less important from the standpoint of proper performance. Plating generally requires the highest degree of surface cleanliness, but even here some types of solutions show a far greater sensitivity toward soil than others. Other finishing operations, such as porcelain enamelling, may be as sensitive as plating to certain types of soil and yet be wholly insensitive to others.

Viewed broadly, therefore, the evaluation of cleaning materials in the metal-finishing industry can be exceedingly complex. Properly speaking, their properties can be defined only with reference to the particular operation in question. In the multiplicity of requirements however, certain general properties recur, some of the most important of which follow: soil removal, retention of cleaning ability in continued use, effect of constituents of the cleaner upon succeeding operations, control of foaming, and corrosion.

The above do not include many properties of importance to metal-cleaning materials, such as toxicity, flammability, effects of water hardness, emulsion stability, etc. They do however represent areas in which evaluation procedures can be most difficult and, if conducted improperly, quite misleading. The following discussion will therefore be limited to the laboratory evaluation of the factors shown with reference to practical plant conditions. A comprehensive review of metal cleaning is contained in an excellent series of bibliographical abstracts prepared by J. C. Harris (5).

#### Soil Removal

An examination of the soil removal properties of a cleaner must satisfy the following requirements: the soil or soils must be representative of those to be re-